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Composition of the essential oils of *Pelargonium sidoides* DC. and *Pelargonium reniforme* Curt.

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ABSTRACT: The essential oils of *Pelargonium sidoides* DC. and *P. reniforme* Curt. were obtained by hydrodistillation from the leaves of the plants in 0.52% and 0.71% yields, respectively, related to the dry weight. Their composition was analysed by GLC and GC–MS. About 230 components have been detected in each of the *Pelargonium* oils, of which 102 (*P. sidoides*) and 81 (*P. reniforme*) could be unambiguously identified, accounting for about 65% and 49% of the total peak area, respectively. For both species, sesquiterpenes (approximately 60%) were the dominating components, with caryophyllene (2.3%) and caryophyllene epoxide (13%) as the most abundant compounds of the sesquiterpene fraction of the oil of *P. sidoides*, and the sesquiterpene hydrocarbons δ-selinene (4.2%) and δ-cadinene (4.0%) as the main representatives of the oil of *P. reniforme*. Other major groups of the oil of *P. sidoides* comprised monoterpenes (16%) and phenylpropanoids (9%), the major compounds of the latter group being methyleugenol (4.3%) and elemicin (3.6%). By contrast, only monoterpenes were found in reasonable amounts (4.7%) in the related species *P. reniforme*. Detection of anacardic acids and furan-type constituents provide a rational explanation for insect deterrency by *Pelargonium* species. © 1998 John Wiley & Sons, Ltd.

KEY WORDS: *Pelargonium sidoides* DC.; *Pelargonium reniforme* Curt; Geraniaceae; essential oil composition; hydrodistillation; GC; GC–MS; insect deterrency

Introduction

Pelargonium species (Geraniaceae) indigenous to areas of southern Africa are traditionally used as an antidiarrhoic and as a general remedy for treatment of colds and infection of the lungs in folk medicine.[1,2] Recent studies demonstrated that *Pelargonium*-containing products have potential therapeutic benefits in these conditions and that coumarins and polyphenolic metabolites are of particular interest, representing the alleged biologically active substances.[3,4]

However, many *Pelargonium* species have a characteristic scent, based on the content of essential oils, which provides for their utilization in perfumery, cosmetic and food applications.[5] Some of the *Pelargonium* essential oils are strongly scented, reminiscent of rosaceous fragrances, and hence are sporadically incorrectly declared in that way. Recently, there has been a considerable interest in the medicinal field in the study of *Pelargonium* essential oils, as a reflection of demonstrated antitumour activities and inhibition of enzymes such as lipoxygenase, prostaglandin synthase and angiotensin-converting enzyme.[6–8] Also worthy of mention is the observation that a trichome exudate, comprising a mixture of anacardic acids and tetrahydropyrans,[9,10] is a potent chemical defence against small pest species, but also that some *Pelargonium* species are effectively repellent to insects and, hence, are widely employed in southern Africa by the native population. From a taxonomic point of view, a chemotaxonomic approach could be useful for both the classification and identification of *Pelargonium* species, in combination with morphological characters, when considering the difficulties in defining, for example, the plant material of the titled species.[11]

Despite these botanic, economic and medicinal facets, as well as the persistent interest of pharmaceutical companies and in perfumery, reflected by numerous papers on geranium oil (*P. graveolens*, hybrids and other *Pelargonium* species),[12–16] detailed studies on the chemical composition of essential oils of distinct *Pelargonium* species are rare.[17–20] In continuation of our study on *Pelargonium* species,[4,11] this paper reports results of the GC–MS analysis of the essential oils of the medicinally used species *P. sidoides* DC. and *P. reniforme* Curt.

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Experimental

Plant Material

The plant material was kindly provided by the pharmaceutical company Dr Willmar Schwabe, Karlsruhe, Germany. The two species of *Pelargonium* were grown in the experimental garden of this company at Staffort. Identification of the plants was conducted by Dr van der Walt, South Africa. Aerial parts were collected from the plants in October 1992 and the harvested material was air-dried at room temperature. A voucher specimen of each plant is deposited at the author's Institute.

Hydrodistillation and Analysis of Volatiles

A total of 290 g dried leaves of each plant sample was subjected to hydrodistillation (4 h) according to the standard procedures described in the DAB 1996 without collector solvent.[21]

The essential oils were analysed using a Hewlett-Packard HP 5790 gas chromatograph equipped with a FID. A DB-Wax fused-silica column (60 m × 0.25 mm i.d., film thickness 0.25 μm) was used for separation with a temperature programme of 60–240°C, at 4°C/min; the injector and detector temperatures were 250°C. Helium was the carrier gas at a flow rate of 1.5 ml/min. Combined GC–MS was carried out on the above gas chromatograph linked to an HP Mass Selective Detector (MSD). The volatiles were identified on the basis of their retention times and mass-spectral fragmentation patterns compared with those of reference compounds stored on the spectrometer database.

Results and Discussion

Microscopic survey of the leaf epidermis of the two *Pelargonium* species under study revealed the presence of numerous glandular trichomes, especially on the lower (abaxial) leaf surface, containing a yellow-green product. The volatile fractions were obtained by hydrodistillation from the dried leaves of *P. sidoides* and *P. reniforme* in 0.52% and 0.71% yields, respectively, on a dry-weight basis. Storage of the strongly aromatic-scented essential oils at 4°C resulted in the precipitation of white materials, which were readily soluble at ambient temperatures.

About 230 components were detected in each of the *Pelargonium* oils, 102 (*P. sidoides*) and 81 (*P. reniforme*) of which were unambiguously identified, accounting for about 65% and 49% of the total peak area, respectively. The majority of the unknown compounds were represented by sesquiterpenes, as concluded from their mass spectral data and their retention times. The components identified in the titled *Pelargonium* species leaf oils are listed, according to their elution order from a DB-Wax column, in Table 1.

For both species, the leaf oil consists of a complex mixture of different substances, with sesquiterpenes (approx. 60%, inclusive of the unknowns) as the dominating components. However, the composition of the essential oil of *P. sidoides* differed significantly from that of *P. reniforme* by the presence of considerable amounts of phenylpropanoids, which were apparently absent or only present as trace components in the latter. Methyleugenol (4.3%) and elemicin (3.6%) were the most abundant phenylpropanoids, accounting for almost 94% of this fraction. This divergence in the essential oil profiles should be of relevance for a clear differentiation of the morphologically closely related *Pelargonium* species.[11] This finding could also be of significance for other *Pelargonium* species, but requires further studies.

With regard to the identified terpenes, a wide range of monoterpenes (hydrocarbons, alcohols, ketones, esters, aldehydes and oxides) and sesquiterpenes (hydrocarbons, oxides and alcohols) was present (Table 1).

Although the composition of the sesquiterpene fraction of the two *Pelargonium* oils was very similar, another distinguishing feature appeared to be the considerably higher percentages of caryophyllene (2.3%) and caryophyllene epoxide (13%) in the oil of *P. sidoides* compared with the amounts of the corresponding volatiles (0.1% and 3.5%, respectively) found in that of *P. reniforme*. On the other hand, the oil of *P. reniforme* was found to contain a relatively high level of sesquiterpene hydrocarbons (19.4% vs. 8.1%) such as α-muurolene (1.2%), cyclosativene (0.9%), calamenene (1.2%), β- (1.2%) and δ-selinene (4.2%), components which were not identified in *P. sidoides*, and fairly high contents of γ- (1.4% vs. 0.5%) and δ-cadinene (4.0% vs. 1.5%). A closer definition of the oxygenated sesquiterpenes revealed similar qualitative and quantitative differences, e.g. in the contents of spathulenol and bisabolol derivatives (Table 1).

The monoterpenes comprised 16.3% and 4.7% of the essential oils, obtained from *P. sidoides* and *P. reniforme*, respectively. In the monoterpene fraction, no significant differences were found regarding the composition of hydrocarbon representatives in the oils under study. The oxygenated monoterpenes constitute the most abundant group (15.3% and 3.8%, respectively) with carvone, geraniol, geranyl acetate, linalyl acetate, linalol, α-terpineol, *p*-mentha-1,5-dien-8-ol and pinocarveol as main components (>0.5%) in the essential oil of *P. sidoides*, while only linalol, geranylacetone and terpinen-4-ol were found in similarly high percentages in that of *P. reniforme* (Table 1). There is a noticeable absence of any monoterpene esters in the essential oil of *P. reniforme*.

Table 1. Volatile compounds in *Pelargonum sidoides* DC. and *P. reniforme* Curt. leaf oils

Compound	Percentage[1]		Compound	Percentage[1]	
	P. sidoides	*P. reniforme*		*P. sidoides*	*P. reniforme*
α-Pinene	tr[2]	–	α-Selinene	0.2	–
α-Thujene	–	0.1	α-Muurolene	–	1.2
Camph-3-ene	–	tr[2]	β-Selinene	–	1.2
β-Pinene	0.1	0.1	Carvone + dihydroagarofuran	–	tr[2]
Sabinene	0.1	–	Carvone	0.7	–
Myrcene	–	tr[2]	Bicyclogermacrene	0.5	–
α-Phellandrene	0.1	–	Naphthalene	–	0.1
α-Terpinene	tr[2]	0.1	1,2-Dihydro-1,1,6-trimethylnaphthalene	–	0.1
Limonene	0.3	0.2	Geranyl acetate	1.9	–
β-Phellandrene	0.1	tr[2]	*n*-Decanol	–	0.1
1,8-Cineole	–	0.1	δ-Cadinene	1.5	4.0
trans-Hex-2-enal	tr[2]	–	γ-Cadinene	0.5	1.4
2-Pentylfuran	–	0.1	Myrtenol	0.5	–
cis-β-Ocimene	tr[2]	–	α-Cadinene	0.1	–
trans-β-Ocimene	tr[2]	–	Deca-2,4-dien-1-al	0.1	–
γ-Terpinene	0.1	0.1	*trans*-Carveol	0.4	–
p-Cymene	0.1	0.3	Calamenene	–	1.2
Isoamyl 3-methylbutanoate	tr[2]	–	Geraniol	0.6	–
Terpinolene	tr[2]	tr[2]	*p*-Cymen-8-ol	–	0.2
Pinon-3-ol	tr[2]	–	Geranylacetone	0.2	0.5
Hept-5-en-2-one	tr[2]	–	*cis*-Carveol	0.1	–
Hexanol	tr[2]	–	Benzyl alcohol	tr[2]	–
cis-Hex-3-enol	tr[2]	–	α-Calacorene	0.4	0.8
Nonanal	tr[2]	–	β-Ionone	0.5	1.2
Fenchone	0.2	–	β-Ionene epoxide	–	0.1
3-(4-Methyl-pent-3-enyl)furan (Perillene)	–	tr[2]	Caryophyllene epoxide	13.1	3.5
			Methyleugenol	4.3	–
α-Thujone	–	0.1	Nerolidol	0.2	0.4
4-Isopropenyltoluene	0.1	–	Octanoic acid	0.3	0.5
cis-Linalol oxide	0.1	0.1	Humulene epoxide	1.1	0.5
β-Thujone	tr[2]	0.1	Cubenol	0.6	1.7
Furfural	tr[2]	–	*epi*-Cubenol	0.1	2.6
α-Cubebene	–	0.5	Cuminol	0.1	0.2
cis-Hex-3-enyl-3-methylbutanoate	0.1	–	Hexahydrofarnesylacetone	1.1	2.3
trans-Linalol oxide	0.1	0.1	Spathulenol	0.3	2.4
Campholenal + 2,4-Heptadienol	0.2	–	Bisaboloxide B	0.6	–
Cyclosativene	–	0.9	β-Bisabolol	0.5	–
α-Copaene	0.2	0.3	Bovolide	0.4	–
Benzaldehyde	0.1	0.1	Nonanoic acid + bovolide	–	0.3
β-Bourbonene	tr[2]	0.2	Eugenol	0.3	–
α/β-Cubebene	–	0.1	T-Cadinol	2.9	1.9
Linalol	0.7	1.1	T-Muurolol	–	0.8
β-Cubebene	–	0.1	γ-Cadinol + carvacrol	0.3	–
Linalyl acetate	0.8	–	δ-Cadinol	–	0.3
p-Menth-2-en-1-ol (*cis* or *trans*)	0.4	–	Methyl 3,7,11-trimethyl-2,6,10 -dodecatrienoate	–	0.5
Octa-3,5-dien-8-one	–	tr[2]			
α-Bergamotene	0.1	–	6-Hexyl salicylic acid	0.2	–
Pinocarvone	0.4	0.1	Methyl hexadecanoate	–	0.6
Hepta-3,5-dien-2-one	–	tr[2]	Cadalene	0.9	1.5
Fenchol	0.2	–	α-Bisabolol	0.4	–
Bornyl acetate	0.2	–	Isospathulenol	0.9	–
β-Elemene	0.2	–	β-Eudesmol	–	0.7
Octa-1,5,7-trien-3-ol	0.1	–	α-Cadinol	1.3	–
Terpinen-4-ol	0.4	0.5	Intermedeol	–	0.4
Caryophyllene	2.3	0.1	*ar*-Turmerone	–	0.3
Salicylaldehyde	–	0.1	Elemicin	3.6	–
Cyclocitral	–	0.2	Decanoic acid	–	1.4
p-Menth-2-en-1-ol (*trans* or *cis*)	0.5	–	Caryophylla-1(12), 15-dien-9-ol	0.9	–
Myrtenal	0.4	0.1	Asarone	0.1	–
Phenylacetaldehyde	0.1	–	*cis*-Lancelyl acetate	2.4	–
allo-Aromandrendrone	0.4	–	Farnesylacetone	0.5	–
Pinocarveol	0.6	0.3	*cis*-Nuciferyl acetate	0.7	–
β-Farnesene	–	0.1	*cis*-Nuciferol	0.1	–
Methylchavicol	0.2	–	Dodecanoic acid	0.6	1.0
p-Mentha-2,8-dien-1-ol	0.1	–	Methyl octadeca-9,12-dienoate	–	0.4
α-Humulene + piperitol	0.7	–	*cis*-Lanceol	0.4	–
Cryptone	–	0.2	Methyl octadeca-9,12,15-trienoate	–	0.2
γ-Muurolene	0.1	–	Phytol	–	0.5
α-Terpineol	1.3	0.2	Benzyl benzoate	–	0.1
δ-Selinene	–	4.2	Octadec-9-enoic acid	–	0.2
Neryl acetate + myrtenyl acetate	0.2	–	Tetradecanoic acid	0.1	–
p-Mentha-1,5-dien-8-ol	1.7	–	Pentadecanoic acid	0.2	–
Germacrene-D	–	0.8	Octadecanoic acid	3.5	–

[1] Quantification according to the area percentage method without consideration of calibration factors (*F*), i.e. $F = 1.0$ for all compounds.
[2] tr < 0.05%.

The presence of glandular trichomes on the lower leaf surface of both *Pelargonium* species is an indication that essential oil components are synthesized and accumulated, as shown by the identification of a series of terpenoid compounds and some phenylpropanoids in the leaf oils. Others, such as the alkane derivatives, the free fatty acids and fatty acid methyl esters (cf. Table 1), are concluded to be constitutents of the epicuticular leaf wax of the *Pelargonium* species examined rather than typical oil constituents. However, fatty acids are the putative precursors of anacardic acids, constituents of the glandular trichome exudate which represent part of the chemical defence arsenal.[9] Interestingly, the presence of methyl esters appeared to be confined to *P. reniforme*. Geranylacetone is considered to be derived from carotenoids.[22] Some minor or trace compounds, found in either of the two oils, are worth mentioning: the rare essential oil C_{13} component 1,2-dihydro-1,1,6-trimethyl-naphthalene,[23] and *trans*-hex-2-enal and *cis*-hex-3-enol, which are usually constituents of leaf oils and are formed when leaves are damaged.[24,25]

Constituents of the phenolic fraction, such as anacardic acids (e.g. 6-hexylsalicylic acid), salicylaldehyde, benzaldehyde and benzyl benzoate, are well known for their implications in interactions between plants and insects.[26] Tentative detection of further anacardic acids via the characteristic salicylic fragment *m/z* 138 and the presence of phenolic compounds with antimicrobial properties in the essential oil of both species provide a rational explanation for insect deterrency. Also, the furan-type constituents identified (furfural, 2-pentylfuran, perillene) and naphthalene derivatives (naphthalene, 1,2-dihydro-1,1,6-trimethyl-naphthalene) are suggested to contribute significantly to plant protection against insects.

In summary, these results not only extend our knowledge of the composition of *Pelargonium* oils, but also provide a sound basis for reported insect deterrency by *Pelargonium* species.

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